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Vibrational Analysis of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ ($0.0 \leq x \leq 0.5$) Glass Ceramic Electrolytes Prepared by Acetic Acid-Assisted Sol-Gel Method

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ABSTRACT

In this study, $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ ($0.0 \leq x \leq 0.5$) was prepared by acetic acid-assisted sol-gel method. The structural properties of NASICON phosphates material with chemical formula $LiTi_2(PO_4)_3$ were observed using the Fourier transform infrared spectroscopy. NASICON is a family of crystalline phosphate with a general network system consisting of PO_4 tetrahedra, thus bands were assigned by vibrations contributed by basic phosphates, in the wavenumber region between 1300 cm^{-1} and 600 cm^{-1}. Experimental spectra indicated that all $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ ($0.0 \leq x \leq 0.5$), heat treated at 600°C and 700°C for 3 hours in air, samples showed the presence of phosphate peaks with shift in frequency as Al^{3+} is substituted into the structure, and with increasing temperatures. Some bands broadened and overlapped causing it hard to analyze the arising bands. It however determined the existence of NASICON structure in all of the samples under study.

Keywords: *NASICON, LATP, glass ceramic, sol-gel, FTIR*

INTRODUCTION

The introduction of high energy density lithium ion battery [1] has been a huge milestone for the innovation and discovery of potential lithium-based battery components, both electrodes and electrolytes. Moreover, with the commercialization of lithium ion batteries by SONY in the 1990s [2], countless volumes of research have been done and reported with the aim to produce better batteries with higher density, stable under ambient conditions, safe for consumers, environmentally benign and, of course, being cost efficient [3]. Focusing on the electrolytes, an all solid-state electrolytes are possible substitute for flammable liquid-based electrolytes [4]. Thus, innovation for solid-state ionic conductors is important. Glass-ceramics has great potential as solid electrolytes applied in such batteries [1].

Lithium-based glass ceramic phosphates with structure similar to that of sodium ion conducting compounds, Na^+ SuperIonic CONductor, which paradoxically is known as NASICON, are excellent lithium ion conductors [5-6]. The NASICON-type structure provides lithium ion mobility forming three dimensional network structures (space group R3c) [7] which enable the glass ceramic electrolyte to achieve high ionic conductivity. One of the most common studied NASICON phosphates is $LiTi_2(PO_4)_3$ has ionic conductivity of 10^{-6} S cm^{-1} at room temperature. It is composed of several numbers of octahedral MO_6 units, where M is the tetravalent cation, Ti, and tetrahedral PO_4 units, which are joined to each other's O corners and forms P-O-M bridges [7]. The joined units can also be described as a covalent $[M_2P_3O_{12}]^-$ skeleton [8]. Attempt to increase the ionic conductivity can be done by partial substitution of cations, M^{III} such as Al, Ga, In, Sc, Y, La, Cr, Fe [9]. The partial substitution changes the chemical formula of $LiTi_2(PO_4)_3$ to $Li_{1+x}M^{III}_xTi_{2-x}(PO_4)_3$. The most conductive compound is $Li_{1.3}M^{III}_{0.3}Ti_{1.7}(PO_4)_3$, with an ionic conductivity up to 10^{-3} Scm^{-1}, where the trivalent cation is either Al or Sc [10]. $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$, abbreviated as LATP, is able to give high ionic conductivity due to its structure whereby, the small sized AlO_6 octahedra accommodates Li cations through its larger spaces [9]. Xu et al. [1] reported an impressive high room temperature ionic conductivity of 10^{-3} Scm^{-1} for $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ glass ceramics, similar with that of LATP as reported by J. Fu (1997) [11].

NASICON structure which is composed of strong P-O bonding is one of the main contributing factors to its high conductive characteristic. The phosphate network can be detected by bands of various vibrations contributed by $[PO_4]^{3-}$ polyanions [10]. The LATP structure is built by corner sharing $Ti(Al)O_6$ octahedral and PO_4 tetrahedral in such a way that the octahedra is surrounded by six tetrahedral, forming Ti-O-P bridges which are also described as a covalent $[M_2P_3O_{12}]^-$ skeleton [7-8]. These octahedral and tetrahedral connections generate interstitial voids or spaces, known as M1 and M2 sites [8-9]. The M1 sites are located between two octahedral, TiO_6, having six coordination of oxygen while M2 sites are located between the ribbons which are formed along the c-axis [8-9]. These sites provide pathways also known as bottlenecks, for the transportation of the conducting mobile ions [7]. M1 sites are filled with cations while M2 sites are empty [12].

Previous work by Xu et. al [1] reported sample preparation of sample by using citric acid as its assisting acid. In this study, however, acetic acid is employed. This study is aimed to determine the vibrational analysis and structural studies of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ ($0.0 \leq x \leq 0.5$) before and after being sintered at 600°C and 700°C for 3 hours in air, using Fourier transform infrared spectroscopy (FTIR). The ionic conductivity and phase analysis studies of the material have been reported elsewhere [4].

EXPERIMENTAL

Sample Preparation

The vitreous $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ ($0.0 \leq x \leq 0.5$) sample was prepared by mixing a stoichiometric amount of $Al(NO_3)_3$ (Bendosen) and TiO_2 (QReC), $LiC_2H_3O_2$ (Sigma) and $NH_4H_2PO_4$(SigmaAldrich) by sol-gel method. The mixture was dissolved in ethanol and kept magnetically stirred for about 24 hours at 60°C. Acetic acid was added slowly to maintain pH of 5. The obtained sol was maintained at 70°C for the release of volatile components. The white colored powder that was achieved was grounded and sintered at 600°C and 700°C for 3 hours in air.

Structural Characterization

The LATP materials were structurally characterized using Perkin Elmer FTIR spectrometer SPECTRUM 2000 at wavenumber region from 1300 cm^{-1} to 600 cm^{-1}. From this spectrum, the effect of Al^{3+} substitution, according to its stoichiometric ratio, was observed.

RESULTS AND DISCUSSION

The six samples prepared, $LiTi_2(PO_4)_3$ $Li_{1.1}Al_{0.1}Ti_{1.9}(PO_4)_3$, $Li_{1.2}Al_{0.2}Ti_{1.8}(PO_4)_3$, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$, $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$, $Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$ are referred to as LATP 0, LATP 1, LATP 2, LATP 3, LATP 4, and LATP 5, respectively. Ti-O-P bonds and phosphates, PO_4 bonds are crucial in the identification of the NASICON-type structure before and after being sintered at 600°C and 700°C. LATP 0 for each sintering temperature is referred as the reference to identify the occupancies of Al^{3+} in the Ti-O-P structure, as Al component was not introduced.

Before Sintering

Figure 1 shows the FTIR spectra of samples before sintering. From this spectrum, the effect of Al^{3+} with different stoichiometric values added to the structure of lithium titanium phosphate was observed. In the present study, the band at 1045 cm^{-1} is probably related to the orthophosphate anion PO_4^{3-} vibrations, which is in good agreement to A. H. Ahmad, A. K. Arof [14]. Upon addition of Al^{3+}, whereby partial substitution of Ti with Al occurred, the orthophosphate band showed a shift to a lower wavenumber (1038 cm^{-1}). This shift might be due to the presence of Al^{3+} in the glass structure causing a complexation by joining into the distorted tetrahedral units. Band spotted at 1145 cm^{-1} in LATP 3 is due to the addition of Al^{3+}, indicating that the Al^{3+} ion has successfully being incorporated in the structure. Furthermore, the wavenumber shifted to a lower wavenumber (1142 cm^{-1}) for LATP 5.

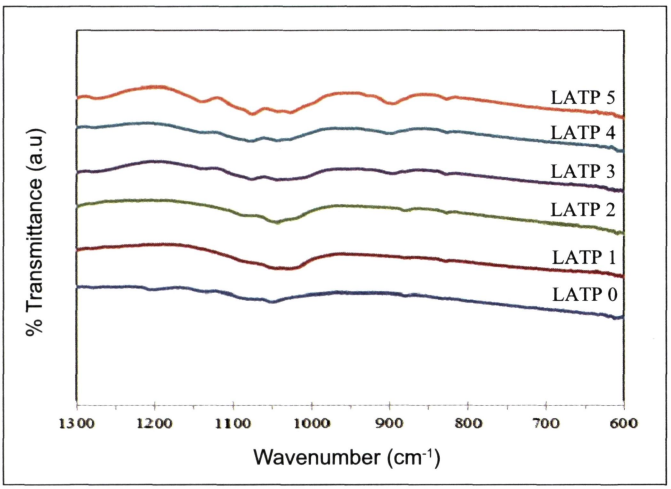

Figure 1: FTIR spectra of LATP 0, LATP 1, LATP 2, LATP 3, LATP 4 and LATP 5, Before Sintering

This might be due to the increasing amount of Al^{3+}. It also explained the shift of PO_4 tetrahedral band and increased intensity and peak size of band around wavenumber 874 cm^{-1} for LATP 0 to 894 cm^{-1} for LATP 5. Bands around 1045 cm^{-1} represented the existence Ti-O-P bonding, thus it can also be said that the addition of Al^{3+} into the material structure resulted in the shift of band to lower wavenumber, which overlapped the band arising from PO_4^{3-} orthophosphate tetrahedral [13].

After Sintering

In order to obtain the NASICON structure for glass ceramic, the samples were sintered at 600°C and 700°C for 3 hours in air. More bands associated with phosphates were expected to be obtained. Figure 2 and Figure 3 show the FTIR spectra of LATP 0, LATP 1, LATP 2, LATP 3, LATP 4, and LATP 5, sintered at 600°C and 700°C for 3 hours in air, respectively. The absorption band attributing to the bending modes of O-P-O can be identified around 613 cm^{-1} for LATP 0 when annealed at 600°C and shifted to a higher wavenumber, 615 cm^{-1} as annealed at 700°C [15]. However, the band broadened as well as increased in band intensity with the increase in annealing temperature. This observation was also observed for all other samples annealed at both temperatures.

This shows that as the samples annealed, the NASICON structure of the glass ceramic joined through corners edge leading to the formation of tunnel-like passage ways. All samples heat treated at temperatures 600°C and 700°C did not show any sign of Al^{3+} band around ~1146 cm^{-1} as compared to before the annealing process. This is probably due to the partial substitution of Al^{3+} into the structure which occurred due to the annealing process.

The band observed at around ~740 cm^{-1} for samples annealed at 600°C and 700°C is attributable to the P-O-P linkage which indicated the presence of PO_4 tetrahedral in the glass ceramics. While bands associated with the asymmetric stretching of PO_4 was observed at 885 cm^{-1} for LATP 0 annealed at 600°C, and shifted significantly to 879 cm^{-1} as annealing temperature increased. This shows that temperature may result in significant changes on the phosphate in the NASICON structure. While for LATP 5, this peak showed obvious intensity decrement and slight shift from frequency 877 cm^{-1} to 879 cm^{-1} with the increase in temperature. The band arising from Ti-O-P was observed for all samples annealed at both temperatures, with bands shifting to lower wavenumber with increasing Al^{3+} intensity, from 1049 cm^{-1} to 1045 cm^{-1} as LATP 0 was sintered at 600°C and 700°C, respectively [13].

The shifting might be due to the partial substitution of Al^{3+} with Ti in the structure of NASICON, which is $LiTi_2(PO_4)_3$. This shift explains the increase in ionic conductivity, as reported elsewhere [4], due to the smaller size of AlO_6 octahedra when compared to TiO_6 octahedra leading to a more appropriate pathway to accommodate the Li^+ mobile ions [9].

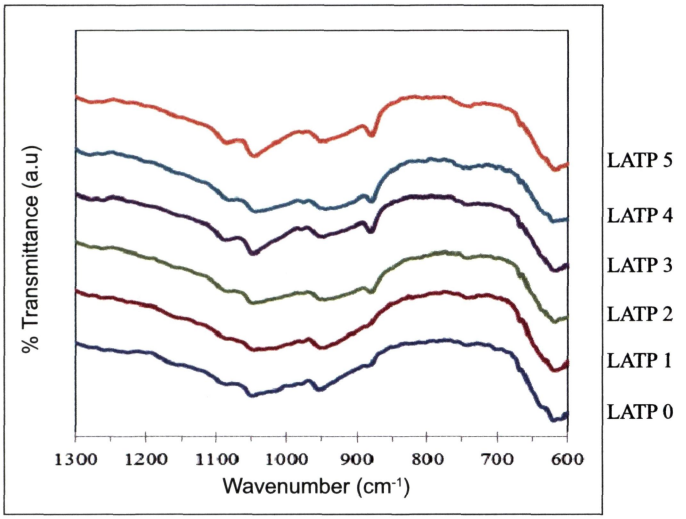

Figure 2: FTIR Spectra of LATP 0, LATP 1, LATP 2, LATP 3, LATP 4 and LATP 5, Sintered at 600˚C for Three Hours in Air

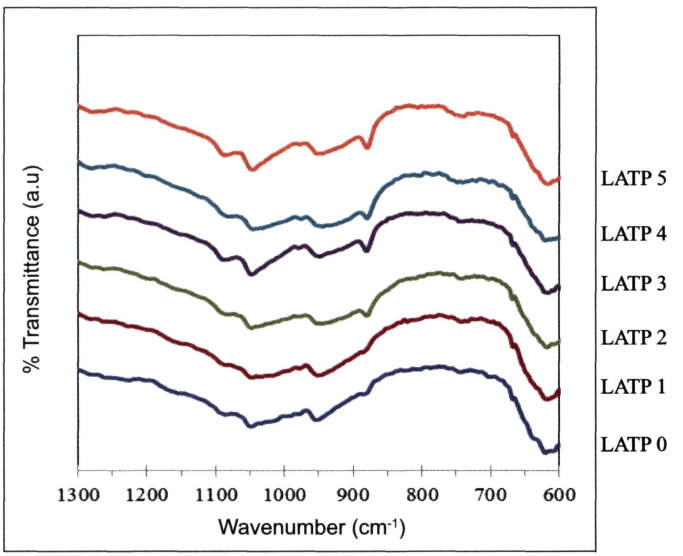

Figure 3: FTIR Spectra of LATP 0, LATP 1, LATP 2, LATP 3, LATP 4 and LATP 5, Sintered at 700˚C for Three Hours in Air

Bands associated with $[PO_4]^{3-}$ [16] were seen at 1087 cm^{-1} for LATP 0 and shifted to 1083 cm^{-1} for LATP 5 with increasing Al^{3+} intensity, as samples annealed at 600°C. As sintering temperature was increased to 700°C, $[PO_4]^{3-}$ band was observed at even a lower frequency, for LATP 0, a significant shift to 1082 cm^{-1} while for LATP 5, a slight shift from 1083 cm^{-1} to 1082 cm^{-1}.

CONCLUSION

The Al^{3+} substitution distorted the structure of NASICON from the studied samples, sintered at 600°C and 700°C. Besides, all samples showed the presence of PO_4 tetrahedral, whereby having NASICON structure provided good lithium ion mobility which is an important aspect in order to achieve high ionic conductivity material.

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